

Electrolyte solutions: from thermodynamic and transport property models to the simulation of industrial processes

Andrzej Anderko*, Peiming Wang, Marshall Rafal

OLI Systems Inc., 108 American Road, Morris Plains, NJ 07950, USA

Received 9 March 2001; accepted 10 August 2001

Abstract

Recent advances in modeling thermodynamic and transport properties of electrolyte solutions are reviewed. In particular, attention is focused on mixed-solvent electrolyte models, equations of state for high-temperature and supercritical electrolyte systems and transport property models for multicomponent, concentrated solutions. The models are analyzed with respect to their capability of computing thermodynamic and transport properties in wide ranges of conditions and composition (i.e. for aqueous or mixed-solvent, dilute or concentrated solutions). Various frameworks for the development of electrolyte models are discussed, i.e. models that treat electrolytes on a completely dissociated or undissociated basis and those that take into account the speciation of solutions. A new mixed-solvent electrolyte model is developed for the simultaneous calculation of speciation and phase equilibria. The role of speciation is discussed with respect to the representation of the thermodynamic properties of mixed-solvent electrolyte solutions and diffusion coefficients in aqueous systems. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrolytes; Model; Excess properties; Equation of state; Electrical viscosity; Diffusion coefficient

1. Introduction

Thermodynamic and transport properties of electrolyte solutions are important for a variety of applications in the chemical process industries. Electrolytes are involved in numerous processes including:

1. Environmental applications such as gas treatment, wastewater treatment or chemical waste disposal;
2. Separation processes such as solution crystallization, extractive distillation, seawater desalination or bioseparations;
3. Electrochemical processes—both undesirable phenomena such as corrosion and industrial processes such as electrolysis;
4. Supercritical technology, including destruction of hazardous agents and synthesis in supercritical fluids;

* Corresponding author. Tel.: +1-973-539-4996; fax: +1-973-539-5922.
E-mail address: aanderko@olisystems.com (A. Anderko).

5. Production of energy sources, including scaling in production wells, utilization of geothermal energy or inhibition of gas hydrate formation;
6. Hydrometallurgical processes.

These applications require models that cover wide ranges of chemical composition (aqueous or mixed-solvent, dilute or concentrated solutions), conditions (ranging from ambient temperatures to supercritical conditions) and physical phenomena that are of interest (e.g. phase equilibria, acid–base equilibria, transport of species to a reacting interface, etc.). Therefore, development of models for electrolyte systems continues to be an important subject of research.

Several excellent reviews of electrolyte solution models are available in the literature. Empirical and semi-empirical models were reviewed by Zemaitis et al. [1], Renon [2], Pitzer [3], Rafal et al. [4] and Loehe and Donohue [5]. Theoretical fundamentals were reviewed by Friedman [6], Conway [7], Mazo and Mou [8] and Loehe and Donohue [5]. These works provide a detailed review of the thermodynamics of aqueous electrolyte systems at temperatures substantially below the critical region. Therefore, we focus in this study on other, less mature, research areas within the realm of electrolyte solutions. These areas include:

1. Models for mixed-solvent electrolyte solutions;
2. Models for supercritical and high-temperature systems involving electrolytes, and
3. Transport property models for multicomponent, concentrated systems.

In these areas, our understanding of physical principles is less advanced than in the area of thermodynamic properties of aqueous electrolytes at “normal” conditions. However, substantial progress has recently been achieved and many practical, engineering-oriented models are currently under development. In this work, emphasis is put on models that are suitable for the simulation of systems encountered in industrial practice. Such models are applicable to multicomponent mixtures over wide concentration and temperature ranges and can be parameterized using available experimental information.

2. Treatment of electrolyte solution chemistry

Before we proceed to analyze selected electrolyte solution models, it is worthwhile to classify them with respect to the method of treating the solution chemistry. Here, the term “solution chemistry” encompasses the chemical equilibria that describe ionic dissociation, ion pair formation, hydrolysis of metal ions, formation of metal–ligand complexes, acid–base reactions, disproportionation reactions, etc. The available electrolyte models can be grouped in three classes, i.e.

1. Models that treat electrolytes on an undissociated basis;
2. Models that assume complete dissociation of all electrolytes into constituent ions;
3. Speciation-based models, which explicitly treat the solution chemistry.

The models that treat electrolytes as undissociated components are analogous to nonelectrolyte mixture models. They are particularly suitable for supercritical and high-temperature systems, in which ion pairs predominate. However, this approach is also used for more typical electrolyte systems at moderate conditions [9–11]. The models that assume complete dissociation are the largest class of models for electrolytes at typical conditions. Compared with the models that treat electrolytes as undissociated or completely

associated, the speciation-based models are more computationally demanding. This is due to the fact that phase equilibrium calculations have to be accompanied by solving chemical equilibria whenever speciation-based models are used. The details of such calculations have been reviewed by Rafal et al. [4]. Also, speciation-based models require the creation of extensive databases containing the properties of various species. In many cases, individual species can be clearly defined and experimentally verified in relatively dilute solutions. At high concentrations, the chemical identity of individual species (e.g. ion pairs or complexes) becomes ambiguous because a given ion has multiple neighbors of opposite sign and, thus, many species lose their distinct chemical character. This becomes particularly evident in the limit of fused salts, which are characterized by an alternating charge pattern [12] rather than the presence of distinct species. Therefore, the application of speciation models to concentrated solutions requires a careful analysis to separate the chemical effects from physical nonideality effects.

When comparing speciation-based models with those that neglect speciation, it is worthwhile to consider the application of the models. If the applications are limited to computing phase equilibria (especially VLE), comparable results can be obtained with models that belong to various classes. For example, the overall activity coefficients and VLE of many transition metal halide solutions, which show appreciable complexation, can be reproduced using Pitzer's ion-interaction approach [3] without taking speciation into account. The advantages of speciation-based models become obvious when other properties are of interest. For numerous applications for which pH is important, speciation models are necessary. The distribution of species (including free and complexed ions) is important for modeling transport phenomena in a variety of electrochemical process (e.g. electrolysis, corrosion) and in natural environments. In multicomponent systems with complicated solution chemistry, speciation is also important for the accurate prediction of solid solubility. This is due to the fact that the distribution of species in multicomponent systems may be different from that in simple single-salt systems, which may in turn affect the solubility and other properties. The knowledge of speciation is also important when some species (e.g. Cr(VI)) are harmful to the environment whereas other species of the same element are relatively benign (e.g. Cr(III)).

In the next section, we briefly review selected models for mixed-solvent electrolyte solutions and outline a new model that was specifically designed to perform speciation calculations.

3. Mixed-solvent electrolyte solutions

Development of thermodynamic models for mixed-solvent electrolyte systems was an active area of research during the last three decades. In general, these models contain several contributions that define the excess Gibbs energy:

1. A long-range force contribution that accounts for electrostatic interactions between ions at high electrolyte dilutions. This contribution is generally represented by the Debye–Hückel [13] or mean spherical approximation theories [14–17].
2. A short-range interaction contribution that includes interactions between all species. Models originally developed for nonelectrolyte solutions, such as NRTL, UNIQUAC, and UNIFAC, have been used for this purpose.
3. The Born model, which represents the electrostatic contribution to ion solvation.

Other approaches include using equations of state based on the Helmholtz energy [18,19,94] rather than the excess Gibbs energy. Table 1 compares some of the thermodynamic models developed in recent

Table 1
Summary of representative activity coefficient models for mixed-solvent electrolyte solutions

Terms ^a	Equilibria	Reference state ^b	Solution chemistry	Features	References
NRTL	VLE (LLE)	$\gamma_u \rightarrow 1$ as $x_u \rightarrow 1$	Undissociated	No LR contribution	[21]
DH + UNIQUAC	VLE	$\gamma_i \rightarrow 1$ as $x_s \rightarrow 1$ & $x_i \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation	Fixed ε ; concentration-dependent UNIQUAC parameters	[27]
DH + UNIQUAC	VLE	$\gamma_i \rightarrow 1$ as $x_s \rightarrow 1$ & $I \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation	Concentration-dependent UNIQUAC parameters	[28]
DH + UNIFAC	VLE	$\gamma_i \rightarrow 1$ as $x_s \rightarrow 1$ & $I \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation		[24]
UNIFAC	VLE, LLE	$\gamma_u \rightarrow 1$ as $x_u \rightarrow 1$	Undissociated	No LR contribution	[11]
DH + MR + UNIQUAC	VLE	$\gamma_1 \rightarrow 1$ as $x_s \rightarrow 1$ & $I \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation	Concentration-dependent MR parameters	[29]
DH + VL + IS	VLE, LLE	$\gamma_1 \rightarrow 1$ as $x_s \rightarrow 1$ & $x_i \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation		[22]
PDH + Born + BG + NRTL	LLE	$\gamma_i \rightarrow 1$ as $x_w \rightarrow 1$ & $x_i \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Speciation	Fixed ε	[20]
NRTL	VLE, SLE	$\gamma_u \rightarrow 1$ as $x_u \rightarrow 1$	Undissociated	No LR contribution	[9,10]
DH + MR + UNIFAC	VLE	$\gamma_i \rightarrow 1$ as $x_s \rightarrow 1$ & $I \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation	Concentration-dependent MR parameters; group interaction parameters in both MR and UNIFAC	[25]
DH + UNIQUAC	VLE, SLE	$\gamma_k \rightarrow 1$ as $x_w \rightarrow 1$ & $x_k \rightarrow 0$; $\gamma_w \rightarrow 1$ as $x_w \rightarrow 1$	Speciation	Using properties of pure water in DH term; also included H^{ex} data	[23]
MSA (GD)	VLE	$\gamma_{\text{st}} \rightarrow 1$ as $x_s \rightarrow 1$ & $x_{\text{st}} \rightarrow 0$; $\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$	Complete dissociation		[30]
MSA + Born + UNIFAC (GD)	VLE	$\gamma_k \rightarrow 1$ as $x_w \rightarrow 1$ & $x_k \rightarrow 0$; $\gamma_w \rightarrow 1$ as $x_w \rightarrow 1$	Speciation		[26]

^a DH = Debye–Hückel, PDH = Pitzer–Debye–Hückel, MR = middle-range, VL = Van Laar, IS = ion-solvation, BG = Bronsted–Guggenheim, GD = Gibbs–Duhem integration.

^b I = ion; st = salt; s = solvent; w = water; u = undissociated species (including solvent); k = all species except water.

years. These models have been generally used for the representation of activities and phase equilibria. Some of these models have been demonstrated to reproduce not only vapor–liquid equilibrium, but also liquid–liquid equilibrium [11,20–22] and solid–liquid equilibrium [9,10,23] in mixed-solvent electrolyte systems. Group contributions were used in some models [11,24–26] to enhance their predictive capability.

Most of the mixed-solvent electrolyte models have been developed on the assumption of complete dissociation of the electrolyte [22,24,25,27–31], or on an undissociated basis [9–11,21,31]. Chemical equilibrium has been treated in some of the models [20,23,26] for selected systems. In many models, the applicability range is limited by the selection of the reference state. In general, a reference state based on the unsymmetrical convention, i.e. infinite dilution in water, limits the applicability of the model to water-dominated systems. The use of different reference states for the solvents and for ions may also cause inconsistency in LLE calculations [11] unless the standard-state of the ionic species is properly selected [20,22].

Several authors have observed that the effect of long-range electrostatic interactions on phase equilibria is negligible at concentrations beyond near-infinite dilution. Therefore, Mock et al. [21], Kolker and de Pablo [9,10], and Dahl and Macedo [11] neglected the long-range interaction contribution in their models and adopted a symmetrical reference state for all species. These models do not show the correct limiting behavior according to Debye–Hückel theory and are not suitable for chemical equilibrium calculations because the electrolyte is assumed to be undissociated.

The available mixed-solvent electrolyte models have not been applied to systems that are continuously miscible from infinite dilution to the fused salt limit. The fused salt limit is becoming increasingly important in view of the interest in room-temperature ionic solvents. Thus, it is desirable to extend the definition of mixed-solvent electrolytes to include liquid salts and to develop thermodynamic models that are capable of reaching this limit.

In the development of mixed-solvent electrolyte models, an important consistency problem arises when a Debye–Hückel expression, originally derived within the McMillan–Mayer (MM) framework, is added to a local composition model derived from the Lewis–Randall (LR) framework [32]. The difference between the activity coefficients, when recalculated from one scale (MM) to another (LR) can be as large as 20% or more for some common salts [33]. When a model is developed by combining a Debye–Hückel term with an excess Gibbs energy model in the LR framework, corrections for scale conversion are necessary to maintain thermodynamic consistency. Mathematical transformations for converting thermodynamic quantities between the MM and LR scales for single- and multi-solvent electrolyte solutions have been developed by Friedman [93], Pailthorpe et al. [34], de Cardoso and O’Connell [32], Cabezas and O’Connell [35], Haynes and Newman [36] and Lee [33]. A Debye–Hückel formalism that is suitable for use in the Lewis–Randall framework has been introduced in the models developed by Macedo et al. [28], Kikic et al. [24], Li et al. [29], Yan et al. [25], and Zerres and Prausnitz [22].

In this study, we present an outline of a new mixed-solvent electrolyte model that is designed to yield comprehensive speciation results in addition to predicting phase equilibria and is valid for systems ranging from infinitely dilute with respect to electrolytes to fused salts. In this model, an expression for the excess Gibbs energy is constructed as a sum of three terms

$$\frac{G^{\text{ex}}}{RT} = \frac{G_{\text{LR}}^{\text{ex}}}{RT} + \frac{G_{\text{MR}}^{\text{ex}}}{RT} + \frac{G_{\text{SR}}^{\text{ex}}}{RT} \quad (1)$$

where $G_{\text{LR}}^{\text{ex}}$ represents the contribution of long-range electrostatic interactions, $G_{\text{SR}}^{\text{ex}}$ is the short-range interaction contribution and an additional (middle-range) term $G_{\text{MR}}^{\text{ex}}$ accounts for ionic interactions that

are not included in the long-range term. In order to cover the entire concentration range for mixed-solvent electrolyte systems (i.e. from a pure solvent to a pure solute, e.g. a fused salt), the new model has been constructed on mole-fraction basis and has been normalized using the symmetrical reference state where $\gamma_i = 1$ as $x_i \rightarrow 1$ for any species. It is obvious that such a reference state is hypothetical for ions. The long-range interactions are represented by the excess function originally developed by Debye and Hückel [13] using the charging process approach [37]:

$$\frac{G_{\text{DH}}^{\text{ex}}}{RT} = -\frac{\kappa}{3\epsilon kT} \sum_{\text{ion}} n_i z_i^2 e^2 \tau(\kappa a) \quad (2)$$

where κ and $\tau(\kappa a)$ are defined by

$$\kappa^2 = \frac{e^2 \sum_i x_i z_i^2}{\epsilon_0 \epsilon kT v}; \quad \tau(\kappa a) = \frac{3}{(\kappa a)^3} \left[\ln(1 + \kappa a) - \kappa a + \frac{(\kappa a)^2}{2} \right] \quad (3)$$

where a is the distance of closest approach between two ions and is set to be 4 Å and v is the molar volume of the mixture. For a realistic representation of the properties of mixed-solvent electrolyte systems, the effect of composition on the dielectric constant must be taken into account. Therefore, ϵ_s is calculated from a general model for the composition dependence of the dielectric constant [38]. Eq. (2) and the resulting expressions for activity coefficients are consistent with those derived for use within the Lewis–Randall framework [22,32].

For the “middle-range” ionic interaction term, a second virial coefficient-type expression is used

$$\frac{G_{\text{MR}}^{\text{ex}}}{RT} = - \left(\sum_i n_i \right) \sum_i \sum_j x_i x_j B_{ij} \quad (4)$$

where the interaction parameter, B_{ij} , is expressed as a function of temperature and ionic strength:

$$B_{ij}(I_x, T) = b_{ij}^{(0)} + (b_{ij}^{(1)} + b_{ij}^{(2)} T) \exp[-(I_x + a_1)^2] + b_{ij}^{(3)} T \quad (5)$$

where $b_{ij}^{(0)}$ through $b_{ij}^{(3)}$ are adjustable parameters and a_1 is set to be 0.01. The short-range interactions are represented by the UNIQUAC local composition model [39]. In most cases, the UNIQUAC parameters are temperature-dependent.

For modeling speciation, accurate representation of chemical potentials of species that participate in chemical reactions is of utmost importance. In aqueous systems, chemical potentials at infinite dilution can be calculated using extensive databases of thermochemical properties (cf. a review by Rafal et al. [4]). For mixed-solvent systems, the correctness of chemical potentials is ensured by combining aqueous standard-state properties with accurately predicted Gibbs energies of transfer. Thus, the activity coefficient model must be constrained to reproduce the Gibbs energies of transfer. The Gibbs energy of transfer of ion i from solvent R to solvent S on molal concentration (m) scale is defined as

$$\Delta_{\text{tr}} G_i^0(\text{R} \rightarrow \text{S})_m = \mu_i^{0,m,\text{S}} - \mu_i^{0,m,\text{R}} \quad (6)$$

where $\mu_i^{0,m,\text{S}}$ and $\mu_i^{0,m,\text{R}}$ are the standard-state (infinite dilution) chemical potentials of ion i in solvent S and R, respectively. Through appropriate thermodynamic manipulation, the standard-state chemical potential of ion i in solvent S can be expressed as

$$\mu_i^{0,m,\text{S}} = \mu_i^{0,m,\text{H}_2\text{O}} + RT \ln \left(\frac{1000}{M_{\text{H}_2\text{O}}} \right) + RT \ln(x_i \gamma_i^{x,\text{H}_2\text{O},\text{S}}) - RT \ln m_i^{\text{S}} \quad (7)$$

where $\mu_i^{0,m,\text{H}_2\text{O}}$ is the standard-state (infinite dilution) chemical potential of ion i in water; m_i^S is the molality of ion i in solvent S, and $\gamma_i^{x,\text{H}_2\text{O},S}$ is the activity coefficient of ion i in solvent S in the unsymmetrical, mole-fraction based convention, which can be calculated using the mixed-solvent electrolyte model. By substituting Eqs. (6) and (7), a general expression is obtained:

$$\Delta_{\text{tr}}G_i^0(\text{R} \rightarrow \text{S})_m = RT \ln \left(\frac{\gamma_i^{x,\text{H}_2\text{O},S} m_i^{\text{R}}}{\gamma_i^{x,\text{H}_2\text{O},\text{R}} m_i^{\text{S}}} \right) \quad (8)$$

At infinite dilution, the Gibbs energy of transfer for an electrolyte C_cA_a from solvent R to S can be obtained by adding those of its constituent cation and anion.

When performing speciation calculations, the activity coefficient model is used in conjunction with standard-state properties of species. In the available databases [4], these properties are defined for infinite dilution in water on the molality basis. Therefore, for chemical equilibrium calculations, the values of activity coefficients based on the symmetrical reference state must be converted to those on the unsymmetrical scale. For this purpose, the mole fraction-based activity coefficient of species k in the symmetrical reference state, γ_k^x , is first converted to that based on the unsymmetrical reference state, i.e. at infinite dilution in water, $\gamma_k^{\infty,x}$, i.e.

$$\ln \gamma_k^{\infty,x} = \ln \gamma_k^x - \lim_{\substack{x_k \rightarrow 0 \\ x_w \rightarrow 1}} \ln \gamma_k^x \quad (9)$$

where $\lim_{\substack{x_k \rightarrow 0 \\ x_w \rightarrow 1}} \gamma_k^x$ is the value of the symmetrical activity coefficient at infinite dilution in water. At the same time, the molality-based standard-state chemical potential, $\mu_k^{\infty,m,0}$ can be converted to a mole fraction-based quantity, $\mu_k^{\infty,x,0}$, by

$$\mu_k^{\infty,x,0} = \mu_k^{\infty,m,0} + RT \ln \left(\frac{1000}{M_w} \right) \quad (10)$$

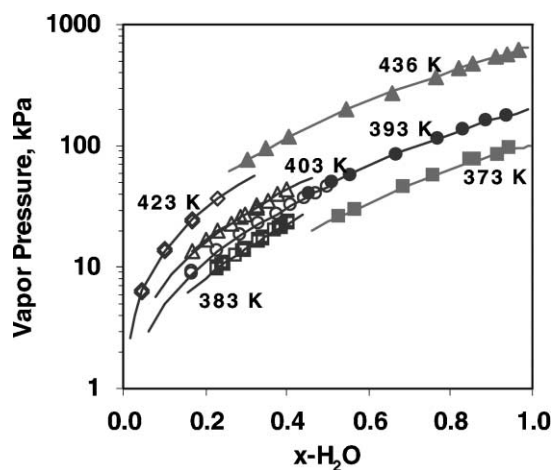


Fig. 1. Computation of vapor pressures for the $\text{LiNO}_3\text{--KNO}_3\text{--H}_2\text{O}$ system as a function of mole fraction of water. The solid symbols are from [77] and the open symbols are from [78,79].

where M_w is the molar weight of water. The unsymmetrical activity coefficient based on Eq. (9) can then be used with the standard-state chemical potential calculated using Eq. (10) for chemical equilibrium calculations. It should be noted that this procedure remains valid even when the system of interest does not contain any water.

The model outlined above is applicable to various classes of systems including (1) aqueous solutions from infinitely dilute to fused salts, (2) electrolytes in mixed organic-water solvents up to solid saturation and (3) partially or fully ionizable systems (e.g. various acids) in the whole concentration range ($x_{\text{acid}} = 0-1$) in water and in organic solvents. For example, Fig. 1 shows the representation of vapor-liquid equilibria for the $\text{LiNO}_3\text{-KNO}_3\text{-H}_2\text{O}$ system over a wide concentration range from pure water to almost the fused salt limit. Solid solubility is also accurately reproduced for this and other systems. Results of modeling speciation effects are shown in Fig. 2 for the acetic acid-water-ethanol system. The dissociation constant of acetic acid in ethanol-water mixtures, which varies as a function of composition by several orders of magnitude, can be very well reproduced as shown in Fig. 2. Fig. 2 also shows the distribution of species in this system. Such results are particularly useful when the acidity of mixed-solvent systems is of

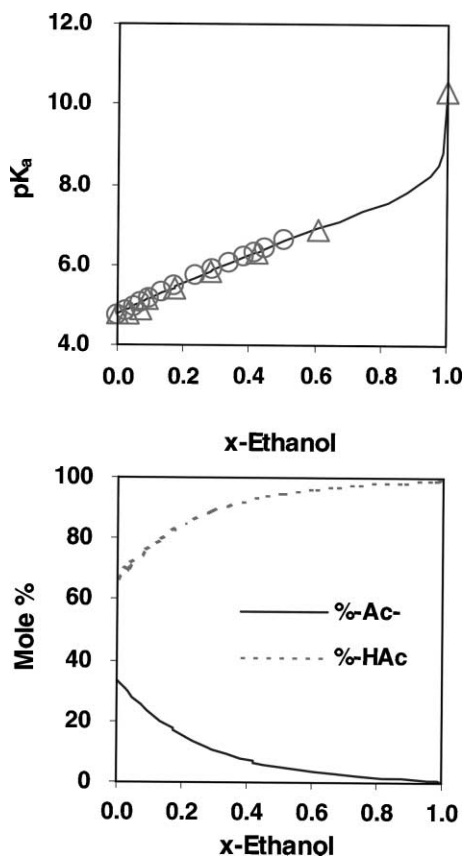


Fig. 2. Speciation of acetic acid in ethanol-water mixtures at 298 K. The upper diagram shows experimental and calculated dissociation constant of acetic acid. The symbols denote the data of Panichajakul and Woolley [80] (○) and, Sen et al. [81] (△). The lower diagram shows the distribution of dissociated and undissociated acetic acid.

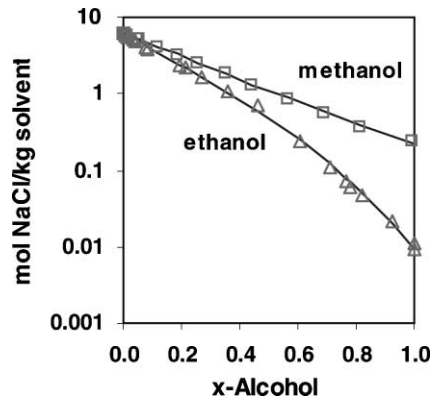


Fig. 3. Calculation of solubility of NaCl(s) in ethanol–water and methanol–water at 298 K. Experimental data are from [31,82].

interest for practical applications. As shown in Fig. 3, the model can accurately reproduce the solubility of salts in alcohol–water systems in the complete concentration range from pure water to pure alcohol.

An issue of particular interest is the inclusion of the Born electrostatic solvation term into a mixed-solvent electrolyte model. The Born model was included in the models of Liu and Watanasiri [20] and Lee [26] to account for the changes in the Gibbs energy of ions due to the change in the dielectric constant. However, it has been found in this study that inclusion of the Born term does not contribute to the accuracy of the model. This is due to the fact that the Born term may give a partial Gibbs energy that is qualitatively incorrect with a wrong sign (cf. [22]). Also, the Born term contribution to the activity coefficient shows a maximum with respect to concentration when the dielectric constant is corrected to account for composition effects. This may result in unreasonable values of the calculated activity coefficients of ionic species. The results obtained with the model described above show that the Gibbs energy of transfer can be accurately reproduced without using the Born term. This indicates that the change in the Gibbs energy of ions that accompanies the transfer of the ion from one solvent to another (which is partly influenced by electrostatic solvation effects) can be reproduced by Eq. (1), i.e. without the Born term.

4. Modeling high-temperature and supercritical systems

Thermodynamic properties of high-temperature and supercritical aqueous systems are important for a variety of applications, including the study of geological systems, power plant engineering and supercritical reaction technology. In particular, the knowledge of phase equilibria in multicomponent systems containing water, salts and nonelectrolytes is needed for the development of supercritical waste oxidation technologies. For such applications, the behavior of aqueous salt systems at temperatures ranging from ca. 300 to ca. 1000 °C are of primary importance. The properties of high-temperature electrolyte solutions are significantly different from those at moderate temperatures because of the strong increase in the tendency for ion pairing as the temperature increases. The predominance of ion pairs is undoubtedly true in the vapor phase and has been demonstrated for the liquid phase using conductance measurements [40,41]. Also, the formation of ion pairs gives rise to substantial concentrations of salts in the vapor phase, which can vary by many orders of magnitude as a function of temperature and pressure. This behavior

becomes particularly evident at temperatures above approximately 300 °C. The need to account for these phenomena makes it necessary to use models that are appreciably different from those that are appropriate at temperature below 300 °C.

During the last decade, several equations of state were developed for the representation of high-temperature electrolyte systems. In particular, Tanger and Pitzer [42] proposed an equation of state for the prototype system NaCl–H₂O on the basis of an expansion around the critical point of water. An equation based on the corresponding-states principle was developed by Levelt-Sengers and Gallagher [43]. These equations were calibrated to reproduce vapor–liquid equilibria for NaCl + H₂O, but failed to predict correct volumetric behavior at liquid-like densities. In contrast, the equation of Lvov and Wood [44] reproduced volumetric data for liquid-like densities over a wide temperature range, but there was no claim with respect to chemical potentials or phase compositions. Anderko and Pitzer [45] developed a more comprehensive equation of state for the representation of vapor–liquid and solid–liquid equilibria as well as volumetric properties of the NaCl–H₂O system. The model of Anderko and Pitzer [45] is based on a reference term that describes the properties of a system containing dipolar ion pairs and solvent molecules. This model was later extended to other salt systems [46–48] and to the mixed system NaCl + H₂O + CO₂ [49]. Economou et al. [50] developed a different equation of state for high-temperature salt systems by combining the ion-paired, dipolar reference system with the previously developed AFACT equation of state. More recently, Kosinski and Anderko [51] extended the Anderko–Pitzer EOS to multicomponent water–salt–nonelectrolyte systems and developed a corresponding-states methodology for systems for which very little experimental information is available. In this section, we briefly analyze this model and identify the areas in which improvement is needed.

To develop a practically-oriented equation of state, it is useful to define a reference part and a perturbation contribution. For high-temperature salt systems, the reference part represents the properties of a mixture of hard-sphere, dipolar or quadrupolar ion pairs and solvent molecules. The perturbation part arises from all other interactions and is expressed by an augmented van der Waals term. Thus, the fundamental expression for the residual Helmholtz energy is written as [45]

$$a^{\text{res}}(T, v, x) = a^{\text{rep}}(v, x) + a^{\text{dip}}(T, v, x) + a^{\text{per}}(T, v, x) \quad (11)$$

where a^{rep} , a^{dip} and a^{per} are the repulsive, electrostatic and perturbation contributions, respectively. A pure substance (either a salt or water or a nonelectrolyte component), is characterized by the dipole moment in the a^{dip} term, the van der Waals attractive parameters in the a^{per} term and the van der Waals co-volume in all three terms. An extension of Eq. (11) to quadrupolar fluids is also available [47]. The a^{per} term also contains binary parameters.

The EOS parameters can be evaluated if sufficient experimental data are available for the mixture of interest. In the case of high-temperature salt–water systems, a comprehensive experimental database exists only for NaCl. Fragmentary VLE, PVT and solubility data are available for KCl, LiCl, CaCl₂ and Na₂SO₄. For most salts, experimental data are limited to solid solubilities or are lacking altogether. Therefore, a two-level approach to parameter evaluation was developed [51]:

1. Parameters for the NaCl + H₂O system were regressed using all available VLE, density and SLE data to create a comprehensive equation of state. Fig. 4 shows the results of vapor–liquid equilibrium calculations for this system for temperatures ranging from 573 to 1073 K.
2. The resulting equation of state for NaCl–H₂O was used as a “master EOS” for other salt–water systems. Only selected parameters were then adjusted to match the behavior of other systems.

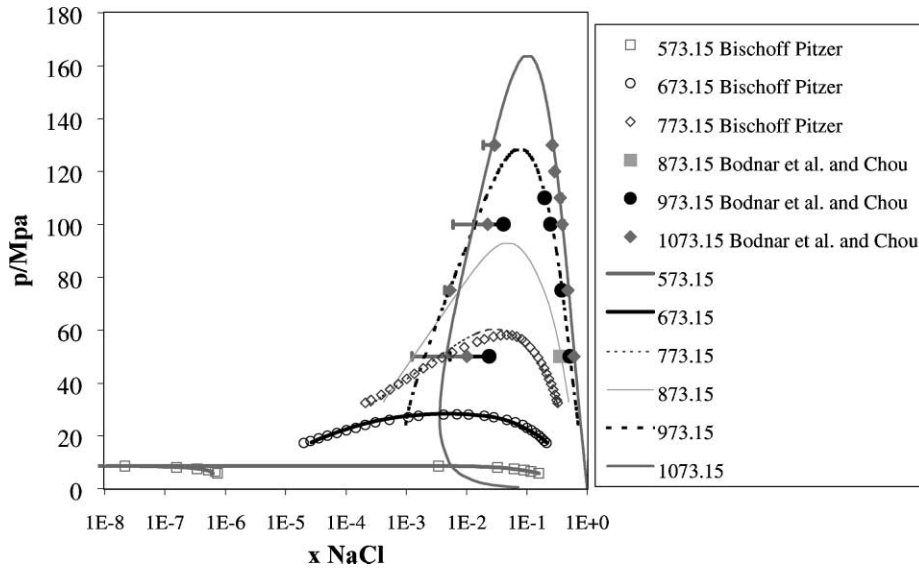


Fig. 4. Computation of vapor–liquid equilibria in the system NaCl–H₂O using the high-temperature EOS. The symbols denote the data of Bischoff and Pitzer [83] and Bodnar et al. [84], as recalculated by Chou [85].

For estimating the properties of systems for which little experimental information is available, a corresponding-states approach is promising. In the case of pure ionic fluids, corresponding-states methods [52–54] have been proven useful for estimating the properties of salts at high temperatures. However, no rigorous corresponding-states treatment is available for salt–water mixtures. At the same time, analysis of the phase behavior of several electrolyte systems at high temperature reveals significant regularities [54,55], which may be regarded as a manifestation of a corresponding-states behavior. For example, the shape of vapor–liquid coexistence curves is similar for aqueous NaCl, KCl and NaOH solutions. This indicates that a mapping transformation can be found that would map the properties of several salts onto the properties of the well-known NaCl + H₂O system. Kosinski and Anderko [51] proposed such a transformation by noting that the EOS (Eq. (11)) can be written in terms of three reduced variables $\tilde{a} = a/a^*$, $\tilde{b} = b/b^*$ and $\tilde{\mu} = \mu/\mu^*$, where the asterisk denotes a reducing parameter, which is substance-specific, but generally unknown. Since the behavior of ion-pair fluids should be the same under the same reduced conditions, the equation of state for an MeX fluid can be mapped onto the equation of state for NaCl by applying a transformation of parameters, i.e.

$$a_{\text{MeX}} = \frac{a_{\text{MeX}}^*}{a_{\text{NaCl}}^*} a_{\text{NaCl}} = k_{\text{MeX,NaCl}}^{(a)} a_{\text{NaCl}} \quad (12)$$

with analogous expressions for the parameters b and m . The three parameters $k_{\text{MeX,NaCl}}^{(a)} a_{\text{NaCl}}$, $k_{\text{MeX,NaCl}}^{(b)} a_{\text{NaCl}}$ and $k_{\text{MeX,NaCl}}^{(\mu)} a_{\text{NaCl}}$ are temperature-independent proportionality factors and the MeX–H₂O binary interaction parameters can be approximated by those for NaCl–H₂O. Thus, the equation of state for the MeX–H₂O fluid can be mapped onto the equation for NaCl–H₂O by adjusting only the three proportionality factors. Fig. 5 illustrates the results of such calculations for the system KCl + H₂O. As

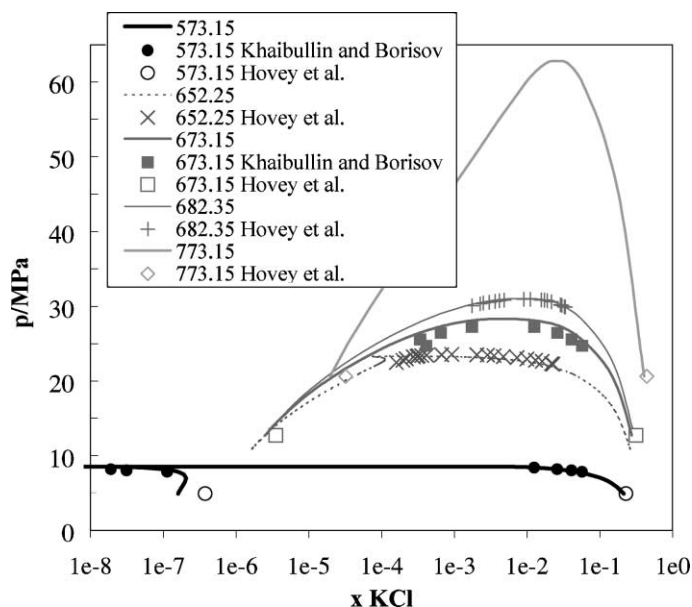


Fig. 5. Vapor–liquid equilibria in the system KCl + H₂O. The lines have been obtained from the EOS for NaCl + H₂O after applying a transformation of parameters. The symbols represent the data of Khaibullin and Borisov [86] and Hovey et al. [87].

shown in this figure, the transformation yields accurate results of vapor–liquid equilibrium calculations for this system.

The transformation of parameters based on corresponding-states considerations applies only to fluid properties. The solid-phase properties remain entirely substance-specific. Thus, when applying the

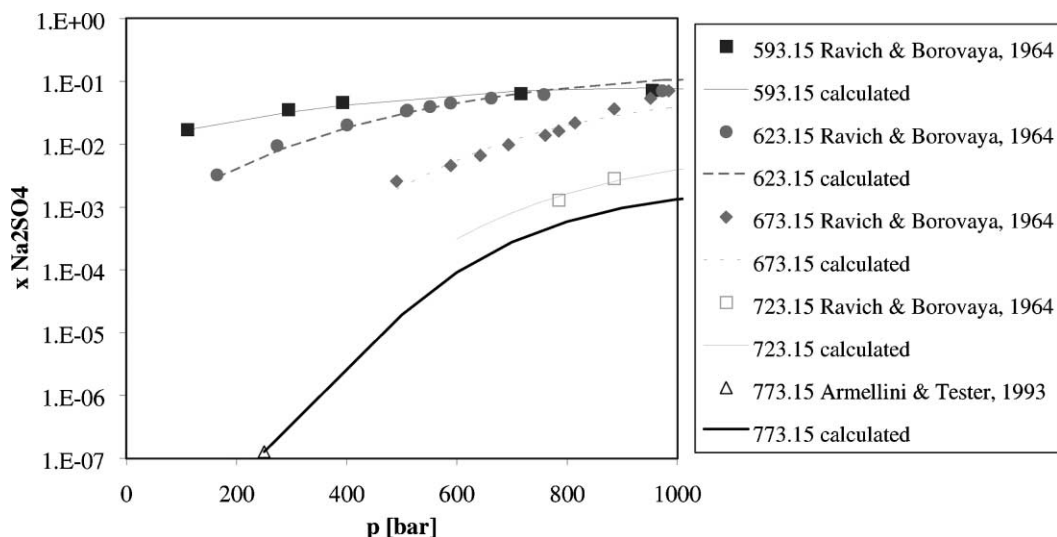


Fig. 6. Solid–fluid equilibria for the system Na₂SO₄ + H₂O. The lines have been obtained from the EOS and the symbols represent experimental data [88,89].

“master” EOS with transformed parameters, it is necessary to use specific parameters for computing solid-phase fugacities, which are necessary to compute solid–fluid equilibria. An example of such calculations is shown in Fig. 6 for the system $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$.

It should be noted that the high-temperature models have not been, so far, used in the framework of speciation calculations. An extension of the high-temperature electrolyte EOS to simulate speciation equilibria would be highly desirable in view of the well-known effects of hydrolysis of salts in supercritical fluids. Also, it would make it possible to model other reactions in supercritical water. The development of a comprehensive, speciation-based equation of state for high-temperature electrolyte systems would require a simultaneous analysis of thermodynamic and electrical conductance data in view of the fact that conductance provides more direct information regarding ion pairing. Another worthwhile goal would be to integrate the high-temperature, ion pair-based approach with the low- and moderate-temperature approach into a unified model. Such a model, if computationally efficient, would span the full range of temperatures that are of interest in practice and would avoid any discontinuities in the prediction of thermodynamic properties.

5. Transport properties of electrolyte solutions

Development of theories of transport properties of dilute electrolyte solutions has been a classical subject of statistical mechanics since the pioneering works of Onsager and Fuoss [56]. Traditionally, the theoretical models have been focused on elucidating the limiting conductivity or diffusivity as a function of ion properties and on predicting the composition dependence of transport properties of dilute solutions.

Limiting conductivities and diffusion coefficients at infinite dilution provide a starting point for the computation of transport properties at finite concentrations. Unlike the finite-concentration properties, the limiting properties are additive with respect to individual ions. The available theories of limiting diffusivity and conductivity are based on the continuum-mechanics dielectric friction approach [57,58]. The dielectric friction theory makes it possible to gain insight into the mobility of charged spheres in a dielectric continuum. However, it does not yield quantitative predictions for real ions because it does not include structural effects of ion–solvent interactions [59,60]. The structural effects caused by interactions between ions and the hydrogen-bonded network of water molecules were extensively investigated using experimental techniques [61,62]. It was determined that the temperature dependence of limiting diffusivities and conductivities is determined by the structure-breaking and structure-making properties of ions. To develop a correlation for predicting the temperature dependence of limiting conductivity and diffusivity, Anderko and Lencka [63,64] utilized the structural entropy of ions, which was proposed by Marcus [65] as a quantitative measure of the structure-making and structure-breaking properties of ions. This correlation makes it possible to predict the limiting conductivity or diffusivity as a function of temperature if one experimental data point is known (usually at ambient temperature).

In the case of viscosity, the properties of individual ions are determined by the Jones–Dole B coefficients [66]. These coefficients determine the concentration dependence of viscosity in relatively dilute electrolyte solutions. From the point of view of their physical significance, the Jones–Dole B coefficients are the analogs of limiting diffusivity or conductivity because they are additive with respect to individual ions and they are influenced by the structural properties of ions [65,67]. Lencka et al. [68] developed a correlation for predicting the temperature dependence of the B coefficients using the values of the entropy of hydration of ions. With this correlation, the B coefficients can be predicted as a function of temperature

if one experimental data point is available at a reference temperature. There is substantial evidence that structural effects determine not only the temperature dependence of the viscosity B coefficients, but also their absolute values. However, a quantitative correlation for the prediction of the B coefficients at a reference temperature has not been found yet.

The concentration dependence of transport properties has been extensively studied for dilute solutions. As early as in 1926, Onsager [69] developed a limiting law for electrical conductivity by using the Debye–Hückel [13] distribution functions. In a comprehensive study, Onsager and Fuoss [56] derived limiting laws for several transport coefficients. This theory was extended to self-diffusivity of ionic mixtures by Onsager and Kim [70]. Justice [71] reviewed various classical theories of electrical conductivity in dilute solutions, which are generally based on coupling Onsager's continuity equations with the Debye–Hückel distribution functions. These theories provide a quantitative representation of the relaxation and electrophoretic effects, which determine the concentration dependence of transport properties in dilute solutions. Because of the limitations of the Debye–Hückel theory, these models are generally valid for concentrations up to 10^{-2} mol/dm³. A major improvement over the classical theories was obtained by Bernard et al. [73] and Turq et al. [74] by combining the Onsager continuity equations with equilibrium distribution functions calculated for the unrestricted primitive model using the mean spherical approximation (MSA). The MSA theory accurately represents the properties of electrolyte solutions in the limit of the primitive model, i.e. up to approximately 1 mol/dm³. This substantially increases the validity range for the transport property predictions. However, analytical expressions for the MSA transport theory are not available for the general case of systems containing multiple cations and anions.

In concentrated electrolyte systems, the concentration dependence of transport properties is determined not only by the electrostatic (relaxation and electrophoretic) effects, which are dominant in relatively dilute solutions. In systems with substantial ionic concentration, the long-range interionic forces are effectively screened to short-range by patterns of alternating charges. Then, interionic forces can be combined with all other interparticle forces on the same basis. Thus, all interparticle forces in concentrated solutions can be effectively treated as short-range forces and the solution properties can be calculated by methods similar to those for nonelectrolytes. This rationale applies to both thermodynamic [12,75] and transport properties. Using this approach, Anderko and Lencka [64] developed a model for self-diffusivity of concentrated electrolyte systems by combining the MSA transport theory with the hard-sphere theory, which is adequate for nonelectrolyte solutions. According to this model, the self-diffusivity is calculated as

$$D_i = D_i^0 \left(\frac{D_i^{\text{HS}}}{D_i^0} \right) \left(1 + \frac{\delta k_i}{k_i} \right) \quad (13)$$

where D_i^0 is the limiting diffusivity and the two terms in parentheses denote the hard sphere and relaxation contributions. For binary systems, the hard-sphere and relaxation terms are calculated from expressions developed by Tham and Gubbins [76] and Bernard et al. [72,73], respectively. Both terms can be computed if the radii of all ions and neutral species are known. To a first approximation, crystallographic radii can be used. In fact, this approximation works for relatively dilute solutions (up to ca. 1 M). For more concentrated solutions, it is necessary to use effective species radii, which are adjusted on the basis of experimental data. Since closed-form expressions for the electrostatic and hard-sphere terms are available only for binary systems, Anderko and Lencka [64] developed a mixing rule based on the Stefan–Maxwell formalism of multicomponent diffusion. An analogous model has also been developed for electrical conductivity [63].

Fig. 7 shows an application of this model to compute the self-diffusivities of all three species that exist in the CaCl₂–H₂O system. The dotted lines in Fig. 7 show the results obtained using only crystallographic

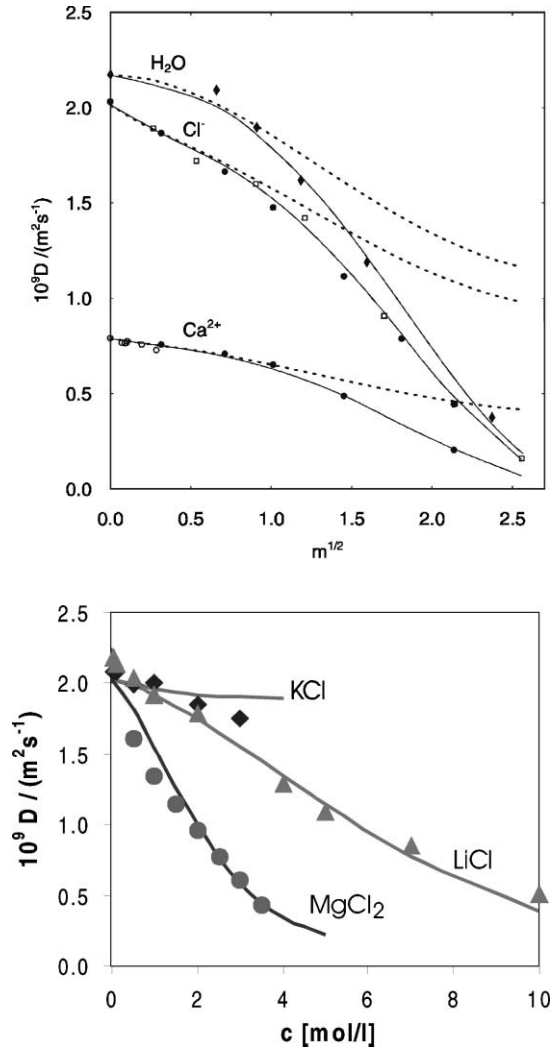


Fig. 7. Self-diffusion coefficients of species in aqueous electrolyte solutions. The upper diagram shows the diffusivities of Ca^{2+} , Cl^- and H_2O in the $\text{CaCl}_2 + \text{H}_2\text{O}$ system. The lines have been obtained from the model using crystallographic ion radii (dotted lines) and effective radii (solid lines). The symbols denote experimental data cited by Mills and Lobo [90], pp. 49–51. The lower diagram compares the diffusivities of oxygen in KCl , LiCl and MgCl_2 solutions with the experimental data of Ikeuchi et al. [91].

diameters. As expected, a reasonable agreement with experimental data has been obtained only for relatively dilute solutions, i.e. for concentrations below 1 m. At higher concentrations, the model with crystallographic parameters fails to reproduce the experimentally observed rapid decrease of diffusivities with concentration. On the other hand, the model with effective ionic diameters (Eq. (4)) reproduces the data with very good accuracy. This is shown by the solid lines in Fig. 7. The model is also applicable to neutral species. This is illustrated in the lower diagram of Fig. 7 for the diffusivities of oxygen in KCl , LiCl and MgCl_2 solutions.

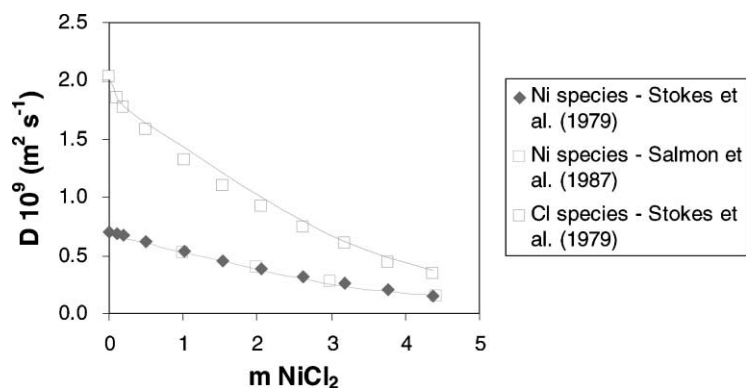


Fig. 8. Calculated and experimental diffusion coefficients for Ni- and Cl-containing species in aqueous NiCl₂ solutions. Experimental data were taken from the compilation of Mills and Lobo [90].

The diffusivity model is consistent with the speciation approach to electrolyte solutions. This is particularly important for systems that show appreciable complexation. In such systems, the measured diffusion coefficients correspond to weighted averages of diffusion coefficients for individual (simple and complexed) species. The measurable aggregate diffusivity of a species that undergoes complexation (denoted by X) is related to those of individual complexes Q_iX_i by [64]

$$D_{X_T} = \sum_i i D_{Q_iX_i} \frac{\partial c_{Q_iX_i}}{\partial c_{X_T}} \quad (14)$$

where the derivative can be computed using a thermodynamic speciation model. For example, Fig. 8 shows the calculated aggregate self-diffusion coefficients of nickel and chloride-containing species in a NiCl₂ solution. Because of the formation of the NiCl⁺ complex, the measured diffusion coefficients of nickel and chloride are not equal to those of bare Ni²⁺ and Cl⁻ ions, respectively (except at infinite dilution). Instead, they include the contribution of complexes according to Eq. (14).

In the case of viscosity, a speciation-based model has been developed by Lencka et al. [68]. This model extends the Jones–Dole [66] equation to multicomponent, concentrated systems. A general expression for the relative viscosity is written as:

$$\eta_r = 1 + \eta_r^{LR} + \eta_r^s + \eta_r^{s-s} \quad (15)$$

where the terms η_r^{LR} , η_r^s and η_r^{s-s} are the contributions of long-range electrostatic effects, individual species and species–species interactions, respectively. The η_r^{LR} term is calculated from the Onsager and Fuoss [56] model for ions in a dielectric continuum. The η_r^s contribution is calculated using the viscosity B coefficients for individual species. Finally, the η_r^{s-s} term is expressed using an empirical function and contains binary parameters that are regressed from experimental data at finite concentration. Fig. 9 shows an application of the viscosity model to LiBr solutions at several temperatures in a relatively wide concentration range.

The transport property models discussed above have been designed to be consistent with the speciation approach. This makes them suitable for modeling electrochemical processes in aqueous systems, in which the transport of individual species is particularly important. However, a major challenge remains to develop extensions of these models to mixed-solvent solutions.

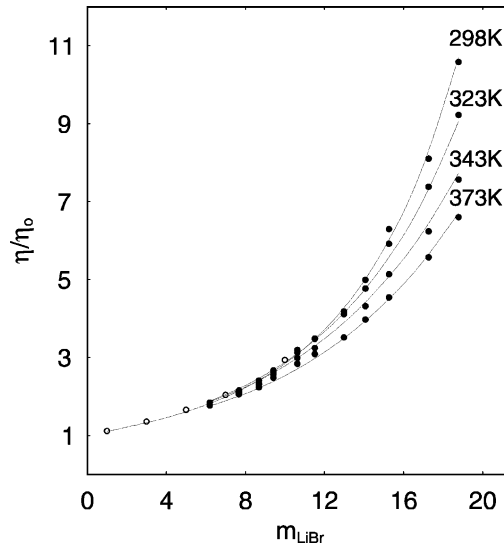


Fig. 9. Comparison of calculated relative viscosities of aqueous LiBr solutions with experimental data of Bogatykh and Evnovich (as cited by Lobo and Quaresma [92]).

6. Conclusions

In recent years, substantial progress has been achieved in the development of semi-empirical, engineering-oriented models for electrolyte solutions. In this review, electrolyte models have been reviewed with emphasis on mixed-solvent electrolyte models, equations of state for high-temperature and supercritical electrolyte systems and transport property models for multicomponent, concentrated systems.

In the area of mixed-solvent electrolytes, efficient activity coefficient models have been obtained by several authors by combining long-range electrostatic interaction terms with short-range interaction terms derived from nonelectrolyte theories. In addition to these terms, a fully quantitative treatment requires the use of additional terms for representing ionic interactions that are not included in the long-range term. It has been demonstrated that it is beneficial to combine excess Gibbs energy models with a comprehensive treatment of solution speciation. A new model has been proposed for this purpose and preliminary results have been obtained. Treatment of speciation for mixed-solvent systems requires a careful combination of standard-state properties with activity coefficient models. This can be achieved in practice by ensuring the correct representation of Gibbs energies of transfer and utilizing the existing databases of standard-state properties in aqueous systems.

In the area of supercritical and high-temperature systems, accurate equations of state have been developed for phase equilibrium computations at temperatures ranging from 300 to 1000 °C. Since these equations are based on the ion-paired reference state, a treatment of speciation and reaction equilibria in high-temperature systems remains to be developed. Another major challenge is to develop a seamless transition between the models that are appropriate in the “normal” temperature range (i.e. up to 300 °C) and the high-temperature models.

In the area of transport properties, engineering-oriented models have been obtained by extending the theories of the transport of ions in a dielectric continuum to multicomponent, concentrated systems. It

has been demonstrated that the predictive character of these models is enhanced when they are combined with thermodynamic speciation calculations. However, extension of transport property models to mixed-solvent systems is not straightforward and remains to be developed.

References

- [1] J.F. Zemaitis Jr., D.M. Clark, M. Rafal, N.C. Scrivner, Handbook of Aqueous Electrolyte Thermodynamics, DIPPR, AIChE, New York, 1986.
- [2] H. Renon, Fluid Phase Equilib. 30 (1986) 181.
- [3] K.S. Pitzer (Ed.), Activity Coefficients in Electrolyte Solutions, 2nd Edition, CRC Press, Boca Raton, FL, 1991.
- [4] M. Rafal, J.W. Berthold, N.C. Scrivner, S.L. Grise, Models for electrolyte solutions, in: S.I. Sandler (Ed.), Models for Thermodynamic and Phase Equilibria Calculations, Marcell Dekker, New York, 1994, p. 601.
- [5] J.R. Loehe, M.D. Donohue, AIChE J. 43 (1997) 180.
- [6] H.L. Friedman, Ann. Rev. Phys. Chem. 32 (1981) 179.
- [7] B.E. Conway, in: B.E. Conway, J.O'M. Bockris, E. Yeager (Eds.), Comprehensive Treatise of Electrochemistry, Plenum Press, New York, 1983, p. 111.
- [8] R.M. Mazo, C.Y. Mou, in: K.S. Pitzer (Ed.), Activity Coefficients in Electrolyte Solutions, 2nd Edition, CRC Press, Boca Raton, FL, 1991 (Chapter 2).
- [9] A. Kolker, J.J. de Pablo, Ind. Eng. Chem. Res. 35 (1996) 228–233.
- [10] A. Kolker, J.J. de Pablo, Ind. Eng. Chem. Res. 35 (1996) 234–240.
- [11] S. Dahl, E.A. Macedo, Ind. Eng. Chem. Res. 31 (1992) 1195–1201.
- [12] K.S. Pitzer, J. Am. Chem. Soc. 102 (1980) 2902.
- [13] P. Debye, E. Huckel, Phys. Z. 24 (1923) 185.
- [14] L. Blum, J.S. Hoye, J. Phys. Chem. 81 (1977) 1311–1316.
- [15] K.L. Gering, L.L. Lee, L.H. Landis, Fluid Phase Equilib. 48 (1989) 111–139.
- [16] T. Cartailier, P. Turq, L. Blum, N. Condamine, J. Phys. Chem. 96 (1992) 6766–6772.
- [17] J.-P. Simonin, L. Blum, P. Turq, J. Phys. Chem. 100 (1996) 7704–7709.
- [18] W. Raatschen, A.H. Harvey, J.M. Prausnitz, Fluid Phase Equilib. 38 (1987) 19–38.
- [19] J.Y. Zuo, D. Zhang, W. Fürst, AIChE J. 46 (2000) 2318–2329.
- [20] Y. Liu, S. Watanasiri, Fluid Phase Equilib. 116 (1996) 193–200.
- [21] B. Mock, L.B. Evans, C.-C. Chen, AIChE J. 32 (1986) 1655–1664.
- [22] H. Zeres, J.M. Prausnitz, AIChE J. 40 (1994) 676–691.
- [23] M.C. Iliuta, K. Thomsen, P. Rasmussen, Chem. Eng. Sci. 55 (2000) 2673–2686.
- [24] I. Kikic, M. Fermeglia, P. Rasmussen, Chem. Eng. Sci. 46 (1991) 2775–2780.
- [25] W. Yan, M. Topphoff, C. Rose, J. Gmehling, Fluid Phase Equilib. 162 (1999) 97–113.
- [26] L.-J.B. Lee, Dissertation, University of Oklahoma, 1996.
- [27] B. Sander, A. Fredenslund, P. Rasmussen, Chem. Eng. Sci. 41 (1986) 1171–1183.
- [28] E.A. Macedo, P. Skovborg, P. Rasmussen, Chem. Eng. Sci. 45 (1990) 875–882.
- [29] J. Li, H.-M. Polka, J. Gmehling, Fluid Phase Equilib. 94 (1994) 89–114.
- [30] R.-S. Wu, L.L. Lee, Fluid Phase Equilib. 78 (1992) 1–24.
- [31] S.P. Pinho, E.A. Macedo, Fluid Phase Equilib. 116 (1996) 209–216.
- [32] M.J.E. de Cardoso, J.P. O'Connell, Fluid Phase Equilib. 33 (1987) 315–326.
- [33] L.L. Lee, J. Mol. Liquid 87 (2000) 129–147.
- [34] B.A. Pailthorpe, J. Mitchell, W.D. Ninham, J. Chem. Soc., Faraday Trans. 2 (1984) 115–129.
- [35] H. Cabezas, J.P. O'Connell, Ind. Eng. Chem. Res. 32 (1993) 2892–2904.
- [36] C.A. Haynes, J. Newman, Fluid Phase Equilib. 145 (1998) 255–268.
- [37] R. Fowler, E.A. Guggenheim, Statistical Thermodynamics, Cambridge University Press, Cambridge, 1956.
- [38] P. Wang, A. Anderko, Fluid Phase Equilib. 186 (2001) 103–122.
- [39] D.S. Abrams, J.M. Prausnitz, AIChE J. 21 (1975) 116–128.
- [40] A.S. Quist, W.L. Marshall, J. Phys. Chem. 72 (1968) 684–703.

- [41] W.L. Marshall, *J. Chem. Soc., Faraday Trans.* 86 (1990) 1807–1814.
- [42] J.C. Tanger IV., K.S. Pitzer, *Geochim. Cosmochim. Acta* 53 (1989) 973–987.
- [43] J.M.H. Levelt-Sengers, J.S. Gallagher, *J. Phys. Chem.* 94 (1990) 7913–7922.
- [44] S.N. Lvov, R.H. Wood, *Fluid Phase Equilib.* 60 (1990) 273–287.
- [45] A. Anderko, K.S. Pitzer, *Geochim. Cosmochim. Acta* 57 (1993) 1657–1680.
- [46] A. Anderko, K.S. Pitzer, *Geochim. Cosmochim. Acta* 57 (1993) 4885–4897.
- [47] S. Jiang, K.S. Pitzer, *AIChE J.* 42 (1996) 585–594.
- [48] J.S. Gallagher, in: *Proceedings of the Presentation at the 13th International Symposium on Thermophysical Properties*, Boulder, CO, 1997.
- [49] Z. Duan, N. Moller, J.H. Weare, *Geochim. Cosmochim. Acta* 59 (1995) 2869–2882.
- [50] I.G. Economou, C.J. Peters, J. de Swaan Arons, *J. Phys. Chem.* 99 (1995) 6182–6193.
- [51] J.J. Kosinski, A. Anderko, *Fluid Phase Equilibria* 183–184 (2001) 75–86.
- [52] H. Reiss, S.W. Mayer, J.L. Katz, *J. Chem. Phys.* 35 (1961) 820–826.
- [53] K.S. Pitzer, *Chem. Phys. Lett.* 105 (1984) 484–489.
- [54] A. Anderko, K.S. Pitzer, *Fluid Phase Equilib.* 79 (1992) 103–112.
- [55] M.I. Ravich, *Water-Salt Systems at Elevated Temperatures and Pressures* (in Russian), Nauka, Moscow, 1974.
- [56] L. Onsager, R.M. Fuoss, *J. Phys. Chem.* 36 (1932) 2689.
- [57] J.B. Hubbard, *J. Chem. Phys.* 68 (1978) 1649.
- [58] J.B. Hubbard, R.F. Kayser, *Chem. Phys.* 66 (1982) 377.
- [59] D.F. Evans, T. Tominaga, J.B. Hubbard, P.G. Wolynes, *J. Phys. Chem.* 83 (1979) 2669.
- [60] K. Ibuki, M. Nakahara, *J. Phys. Chem.* 91 (1987) 4411.
- [61] R.L. Kay, D.F. Evans, *J. Phys. Chem.* 70 (1966) 2325.
- [62] R.L. Kay, G.P. Cunningham, D.F. Evans, in: A.K. Covington, P. Jones (Eds.), *Hydrogen-Bonded Solvent Systems*, Taylor & Francis, London, 1968, p. 249.
- [63] A. Anderko, M.M. Lencka, *Ind. Eng. Chem. Res.* 36 (1997) 1932–1943.
- [64] A. Anderko, M.M. Lencka, *Ind. Eng. Chem. Res.* 37 (1998) 2878–2888.
- [65] Y. Marcus, *Ion Solvation*, Wiley, New York, 1985.
- [66] G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [67] M. Kaminsky, *Z. Phys. Chem.* 12 (1957) 206.
- [68] M.M. Lencka, A. Anderko, S.J. Sanders, R.D. Young, *Int. J. Thermophys.* 19 (1998) 367–378.
- [69] L. Onsager, *Phys. Z.* 27 (1926) 388.
- [70] L. Onsager, S.K. Kim, *J. Phys. Chem.* 61 (1957) 215.
- [71] J.-C. Justice, in: B.E. Conway, J.O'M. Bockris, E. Yeager (Eds.), *Comprehensive Treatise of Electrochemistry*, Vol. 5, Plenum Press, New York, 1983 (Chapter 3).
- [72] O. Bernard, W. Kunz, P. Turq, L. Blum, *J. Phys. Chem.* 96 (1992) 3833.
- [73] O. Bernard, W. Kunz, P. Turq, L. Blum, *J. Phys. Chem.* 96 (1992) 398.
- [74] P. Turq, L. Blum, O. Bernard, W. Kunz, *J. Phys. Chem.* 99 (1995) 822.
- [75] K.S. Pitzer, J.M. Simonson, *J. Phys. Chem.* 90 (1986) 3005.
- [76] M.K. Tham, K.E. Gubbins, *J. Chem. Soc., Faraday Trans.* 1 68 (1972) 1339.
- [77] J.M. Simonson, K.S. Pitzer, *J. Phys. Chem.* 90 (1986) 3009–3013.
- [78] T.B. Tripp, J. Braunstein, *J. Phys. Chem.* 73 (1969) 1984–1990.
- [79] T.B. Tripp, *J. Chem. Thermodyn.* 7 (1975) 263–269.
- [80] C.C. Panichajakul, E.M. Woolley, *Thermodynamic behavior of electrolytes in mixed solvents*, in: W.F. Furter (Ed.), *Advances in Chemistry Series*, Vol. 155, American Chemical Society, Washington, DC, 1976.
- [81] B. Sen, R.N. Roy, D.A. Johnson, L.H. Adcock, *Thermodynamic behavior of electrolytes in mixed solvents: II*, in: W.F. Furter (Ed.), *Advances in Chemistry Series*, Vol. 177, American Chemical Society, Washington, DC, 1979.
- [82] F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, 4th Edition, Vol. II, American Chemical Society, Washington, DC, 1965.
- [83] J.L. Bischoff, K.S. Pitzer, *Am. J. Sci.* 289 (1989) 217–248.
- [84] R.J. Bodnar, C.W. Burnham, S.M. Sterner, *Geochim. Cosmochim. Acta* 49 (1985) 1861–1873.
- [85] I.-M. Chou, *Geochim. Cosmochim. Acta* 51 (1987) 1965–1975.
- [86] I.Kh. Khaibullin, N.M. Borisov, *High Temperature-USSR* 4 (1966) 489–494.

- [87] J.K. Hovey, K.S. Pitzer, J.C. Tanger IV., J.L. Bischoff, R.J. Rosenbauer, *J. Phys. Chem.* 94 (1990) 1175–1179.
- [88] M.I. Ravich, F.E. Borovaya, *Russ. J. Inorg. Chem.* 9 (1964) 520–532.
- [89] F.J. Armellini, J.W. Tester, *Fluid Phase Equilib.* 84 (1993) 123–142.
- [90] R. Mills, V.M.M. Lobo, *Self-Diffusion in Electrolyte Solutions*, Elsevier, Amsterdam, 1989.
- [91] H. Ikeuchi, M. Hayafuji, Y. Aketagawa, J. Taki, G. Sato, *J. Electroanal. Chem.* 396 (1995) 553–556.
- [92] V.M.M. Lobo, J.L. Quaresma, *Handbook of Electrolyte Solutions, Parts A and B*, Elsevier, Amsterdam, 1989.
- [93] H.L. Friedman, *J. Solution Chem.* 1 (1972) 387–417, 419–431
- [94] H.-G. Simon, H. Kistenmacher, J.M. Prausnitz, D. Vortmeyer, *Chem. Eng. Process.* 29 (1991) 139–146.